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Journal of the European Ceramic Society 28 (2008) 2605–2609
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Effects of composition tailoring on structure and microwave dielectric characteristics of $SrSmAlO_4$ ceramics

M.M. Mao, X.C. Fan, X.M. Chen *

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received 18 November 2007; received in revised form 20 March 2008; accepted 28 March 2008
Available online 29 May 2008

Abstract

Effects of composition tailoring on the microwave dielectric characteristics of $SrSmAlO_4$ ceramics were investigated together with the structure. K_2NiF_4-type major phase with minor amount of secondary phases was observed in the modified ceramics with nominal composition $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ($x = -0.05$, -0.025, 0.025, 0.05), and the type of secondary phase is dependent on x. $Sr_{2.25}Sm_{0.75}AlO_{4.875}$ secondary phase is detected for $x > 0$, while the secondary phase for $x < 0$ is $SrSm_2Al_2O_7$. Though the accurate stoichiometric composition is very important to guarantee the highest *Qf* value, it is an effective way to adjust the temperature coefficient of resonant frequency τ_f by tailoring composition. τ_f can be adjusted from negative to positive by varying x from 0 to -0.05, while more negative τ_f can be achieved by varying x from 0 to 0.05. Suitable modified composition with $x < 0$ is also desired for obtaining high *Qf* value and small τ_f with the controlled sensitivity to sintering temperature.

Keywords: $SrSmAlO_4$; K_2NiF_4 structure; Microwave dielectric characteristics

1. Introduction

Recently, a number of microwave dielectric ceramics have been proposed and investigated in $MRAlO_4$ (M = Sr and Ca, R = La, Nd, Sm and Y) with tetragonal K_2NiF_4 structure,[1–3] for which their single crystals were widely used previously as substrates for high-T_c superconducting films.[4–6] In $SrRAlO_4$ system, the tetragonal K_2NiF_4 structure is stable for R = La, Nd and Sm,[1,2] while the stable tetragonal K_2NiF_4 structure is obtained for R = Nd, Sm and Y in $CaRAlO_4$ system.[3] The temperature stable dielectric constant of 18–19 combined with a high *Qf* value (~56,000 GHz) were obtained in the present systems at 10 GHz, and the great potential of improvement in *Qf* by controlling the microstructures was suggested by the previous work.[1–3] Considering the developing trend of low cost in microwave dielectric ceramics,[7] $MRAlO_4$ ceramics without noble elements such as Ta and Nb are expected as very competitive ultra-low loss microwave materials compared with the previous materials such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ (Ref. 8), $Ba(Zn_{1/3}Ta_{2/3})O_3$ (Ref. 9) and $Ba(Zn_{1/3}Nb_{2/3})O_3$ (Ref. 10).

On the other hand, the modified compositions have been widely investigated to improve the giant magnetoresistivity in the ceramics with K_2NiF_4 structure, such as $Sr_{2-x}La_xMnO_4$ and $Sr_{2-x}Nd_xMnO_4$.[11,12] Also, significant effect of nonstoichiometry through adjusting composition upon microwave dielectric properties has been reported for $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics.[13] Therefore, the investigation by composition tailoring in $MRAlO_4$ ceramics is very interesting.

In the present work, the ceramics with nominal composition $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ($x = -0.05$, -0.025, 0, 0.025, 0.05) are prepared and characterized, and the effects of composition tailoring on the microwave dielectric characteristics of $SrSmAlO_4$ ceramics are investigated together with the structure.

2. Experimental procedure

$Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ($x = -0.05$, -0.025, 0, 0.025, 0.05) ceramics were prepared by a solid-state reaction process, using high-purity $SrCO_3$ (99.9%), Sm_2O_3 (99.9%), and Al_2O_3 (99.99%) powders as the raw materials. The weighed raw materials were mixed, by ball milling with zirconia media, in ethanol for 24 h. The mixtures were calcined at 1250 °C in air for 3 h after drying. The calcined powders, with 7 wt% added PVA (polyvinyl alcohol), were pressed into disks of 12 mm in

* Corresponding author.
E-mail address: xmchen59@zju.edu.cn (X.M. Chen).

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doi:10.1016/j.jeurceramsoc.2008.03.031

diameter and 2–6 mm in height. Then these disks were sintered at 1450–1550 °C in air for 3 h. After cooling from the sintering temperature to 1100 °C at a rate of 2 °C/min, the sintered disks were further cooled inside the furnace. The bulk density of sintered disks was measured by the Archimedes method. The phase constitutions of crushed and ground powders of sintered samples were determined by powder X-ray diffractometry (XRD), using Cu Kα radiation. The backscattered electron micrographs were observed for the polished and thermal-etched surfaces of sintered samples by scanning electron microscopy, SEM (JEOL, JSM-5610LV, Japan). The samples were thermally etched for 20 min at the temperature 100 °C below the sintering temperature. The average grain size of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics were obtained by measuring the average linear intercept from their SEM micrographs.[14]

The microwave dielectric constant ε and the temperature coefficient of resonant frequency τ_f were measured using the Hakki–Coleman method.[15] The variation of resonant frequency is plotted as a function of temperature and τ_f is evaluated from the slope of the plots using the equation

$$\tau_f = \frac{1}{f_0}\frac{\Delta f}{\Delta T}$$

where f_0 is the resonant frequency and Δf is the change in frequency during a temperature interval ΔT. In order to obtain accurate results for high Q materials, the quality factor Q (the inverse of the dielectric loss, $\tan\delta$) of the samples was evaluated in resonant-cavity method under microwave frequency.[16,17] Because the Q-factor generally varies inversely with frequency (f) in the microwave region, the product Qf, rather than Q alone, was used to evaluate dielectric loss.

3. Results and discussions

As shown in Fig. 1, the dense ceramics are obtained at sintering temperatures between 1500 °C and 1550 °C, where the relative density reaches to 93%–99% T.D.(theoretical density). XRD patterns of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ($x = -0.05$, -0.025, 0, 0.025, 0.05) ceramics sintered at 1500 °C are shown in Fig. 2. The patterns in accordance with JCPD cards

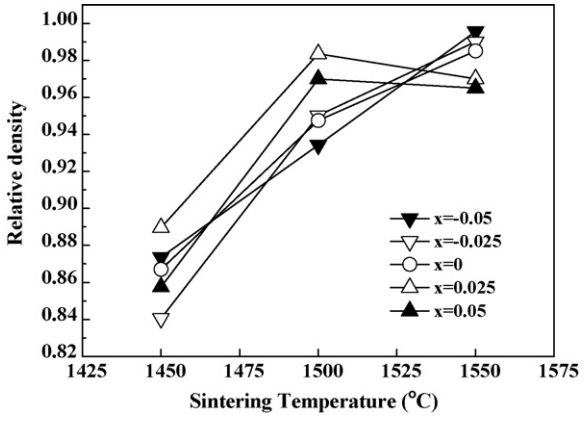

Fig. 1. Relative density of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x and sintering temperature.

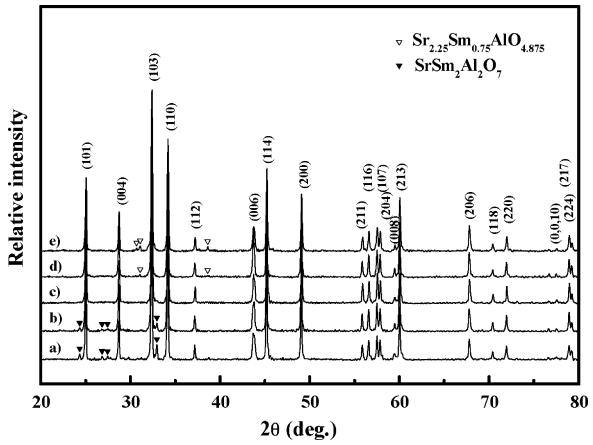

Fig. 2. XRD patterns of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics sintered at 1500 °C: (a) $x = -0.05$, (b) $x = -0.025$, (c) $x = 0$, (d) $x = 0.025$, and (e) $x = 0.05$.

for $SrSmAlO_4$ (JCPD Card No. 24-1190) were marked by the relevant indices of crystallographic plane. K_2NiF_4-type major phase with minor amount of secondary phases was observed in the modified ceramics with nominal composition $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$, and the type of secondary phase is dependent on x. $Sr_{2.25}Sm_{0.75}AlO_{4.875}$ (JCPD Card No. 54-0231) secondary phase is detected for $x > 0$, while the secondary phase for $x < 0$ is $SrSm_2Al_2O_7$ whose patterns are nearly the same to those of $SrGd_2Al_2O_7$ (JCPD Card No. 76-0095).

Electron backscattered micrographs were used as the complementary means to determine the phase constitution of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics (see Fig. 3). For the samples sintered at 1500 °C, the single-phase structure is confirmed for the stoichiometric composition, and it is easy to observe the existence of the secondary phase for the present modified ceramics. Some white spots distributed on the background with a sharp contrast for $x = -0.05$ and -0.025, while the contrast is weak for $x = 0.025$ and 0.05. For the samples sintered at the higher temperature (1550 °C), the excess grain growth and inhomogeneous microstructure are detected for $x > 0$. However, no observed grain size change is detected for the samples of $x < 0$ sintered at 1550 °C. It indicates that the composition tailoring ($x < 0$) suppresses the sintering temperature sensitivity of grain size. Moreover, the precipitation of secondary phase (in white color) is detected for $x = 0$, where single-phase structure is obtained in the ceramics sintered at 1500 °C. But the XRD can hardly detect the peaks for the existence of few quantities of the secondary phase limited by its accuracy. EDAX analysis suggests that the secondary phase might be $SmAlO_3$.

Fig. 4 shows the microwave dielectric constant of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x and sintering temperature. Dielectric constant around 19 is obtained for the $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics sintered at 1500–1550 °C. Qf value of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x and sintering temperature is presented in Fig. 5. Qf value reaches the maximum (69,500 GHz) for the stoichiometric composition sintered at 1500 °C. It is greatly improved compared to the previous results (56,000 GHz).[1] However, a much lower Qf value for $x > 0$ is obtained because of the harmful effect of the sec-

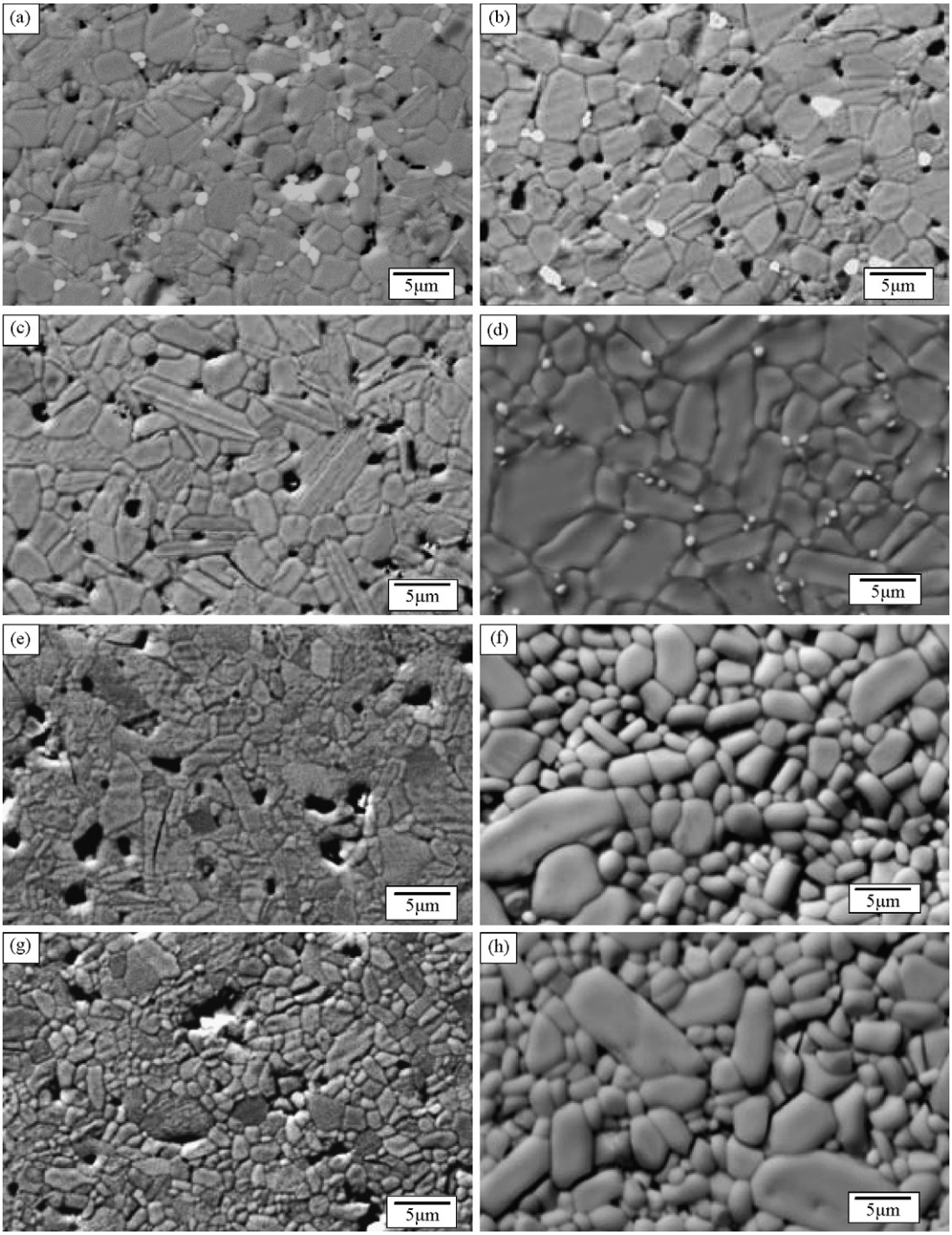

Fig. 3. Backscattered electron images of polished and thermal-etched surfaces of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics sintered at 1500 and 1550 °C in air for 3 h: (a) $x = -0.05$, 1500 °C, (b) $x = -0.025$, 1500 °C, (c) $x = 0$, 1500 °C, (d) $x = 0$, 1550 °C, (e) $x = 0.025$, 1500 °C, (f) $x = 0.025$, 1550 °C, (g) $x = 0.05$, 1500 °C, and (h) $x = 0.05$, 1550 °C.

ondary phase $Sr_{2.25}Sm_{0.75}AlO_{4.875}$. Whereas, the negative effect of $SrSm_2Al_2O_7$ secondary phase in samples with $x < 0$ is relatively weak, and the *Qf* value keeps above 60,000 GHz. For the stoichiometric composition, *Qf* value drops significantly at a higher sintering temperature of 1550 °C primarily due to the secondary phase. Similarly, a much reduced *Qf* value is acquired for $x > 0$, and it is strongly dependent on the sintering temperature. Moreover, the significant decrease in *Qf* value in samples with $x > 0$ sintered at 1550 °C is mainly attributed to the inhomogeneous microstructure with abnormally grown coarser grains (see Fig. 3). However, the high *Qf* value (>60,000 GHz) for $x < 0$ is not sensitive to the sintering temperature because of the uniform fine microstructure with slight sensitivity to sintering temperature. Therefore, it is beneficial to obtain high *Qf* value in a wider range of sintering temperature by tailoring composition ($x < 0$) in $SrSmAlO_4$ ceramics.

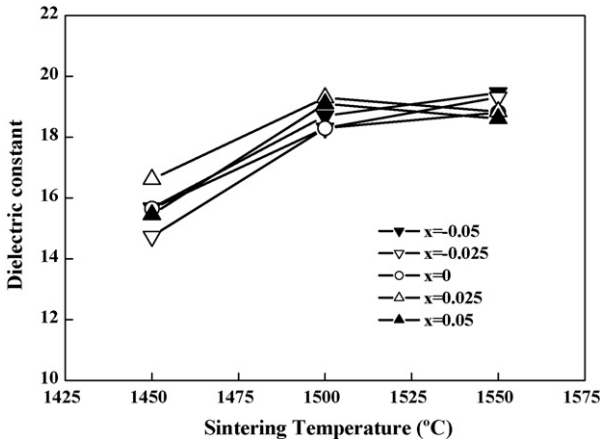

Fig. 4. Microwave dielectric constant of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x and sintering temperature.

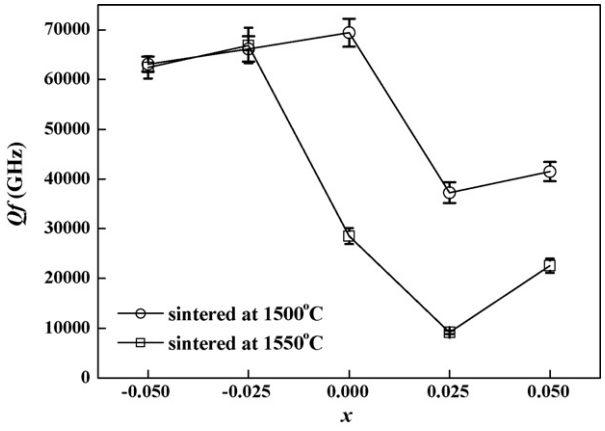

Fig. 5. Qf value of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x.

Fig. 6 displays τ_f of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x and sintering temperature. τ_f generally turns to vary toward positive with increasing $|x|$, and the only exception is the composition of $x=-0.025$ sintered at 1500 °C. Moreover, τ_f is not sensitive to sintering temperature for $x<0$, while different sintering temperatures lead to large variation in τ_f for $x\geq 0$. The variation tendency of τ_f with x and sintering temperature is a combined result of the possible grain orientation and the secondary phase. The obvious anisotropic morphology is observed for the stoichiometric $SrSmAlO_4$ ceramics (see Fig. 3). The grain orientation to some extent is generally expected and a higher sintering temperature should lead to more orientation. By tailoring composition in $SrSmAlO_4$ ceramics, the anisotropic morphology is obviously suppressed. This suggests that the variation of τ_f towards positive by composition tailoring and sintering at a lower temperature can be linked with the suppressed anisotropic morphology and the subsequent grain orientation. The sharp decrease of τ_f towards negative for the stoichiometric composition sintered at 1550 °C is also due to the precipitation of $SmAlO_3$ secondary phase which indicates a large negative τ_f (−74 ppm/°C).[18] Though the data of τ_f are lack for $Sr_{2.25}Sm_{0.75}AlO_{4.875}$ and $SrSm_2Al_2O_7$, the τ_f for such secondary phases might not be much different from that for $SrSmAlO_4$.

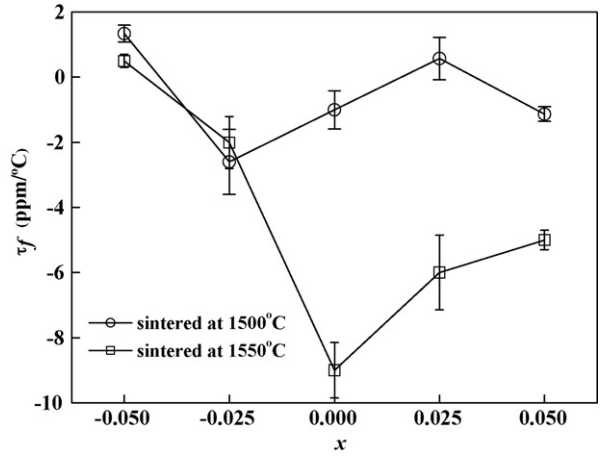

Fig. 6. τ_f of $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ceramics as function of x.

4. Conclusions

Composition tailoring has significant effects on the microwave dielectric characteristics of $SrSmAlO_4$ ceramics. K_2NiF_4-type major phase with minor amount of secondary phases is observed in the modified ceramics with nominal composition $Sr_{1+x}Sm_{1-x}AlO_{4-x/2}$ ($x=-0.05$, -0.025, 0.025, 0.05), and the type of secondary phase is dependent on x. $Sr_{2.25}Sm_{0.75}AlO_{4.875}$ secondary phase is detected for $x>0$, while the secondary phase for $x<0$ is $SrSm_2Al_2O_7$. Though the accurate stoichiometric composition is very important to guarantee the highest Qf value, it is an effective way to adjust the temperature coefficient of resonant frequency τ_f by composition tailoring. τ_f can be modified from negative to positive by varying x from 0 to −0.05. The modified composition with $x<0$ can also reduce the sensitivity of both Qf value and τ_f to sintering temperature, and it is desired for obtaining high Qf value and small τ_f with ease.

Acknowledgements

The present work was supported by the National Science Foundation under grant no. 50332030 and Chinese National Key Project for Fundamental Researches under grant no. 2002 CB613302.

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